EPA Using Surrogate Recoveries in Estimating Analytical Bias

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1 Introduction

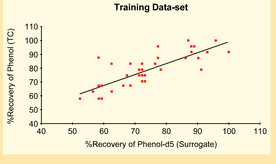
- EPA methods routinely use surrogate compounds in the analysis of semi-volatile target compounds. Surrogates are quality control compounds added to represent the analytical behavior of target compounds. For example, eight surrogate compounds, phenol-d5, 2-fluorophenol, 2-chlorophenol-d4, 1,2-dichlorobenzene-d4, nitrobenzene-d5, 2-fluorobiphenyl, 2,4,6-tribromophenol, and terphenyl-d14, are utilized in the CLP method for semi-volatile analysis.
- The surrogate recoveries in each analysis are used for quality control because they indicate errors or potential problems in the recovery of target compounds through extraction, sample cleanup, extract concentration steps, and analysis.
- The recovery limits for each surrogate are specified by each analytical method and these limits are used for data validation.
- At present, surrogate recovery information is used only qualitatively (as pass/fail criteria) and therefore, is underutilized.
- Surrogate compounds, in general, reflect the analytical behavior of chemically similar target compounds. Therefore, it may be possible to derive quantitative information from surrogate recoveries.
- An earlier study has shown that the recovery of many semi-volatile target compounds is correlated with the recoveries of one or more surrogate compounds (Garner et al. 1988).
- It is possible, therefore, to estimate the bias for many target compounds in each analysis from the recoveries of the surrogates.
- The goal of this study is to assess the effectiveness of such bias estimates.

2 Approach

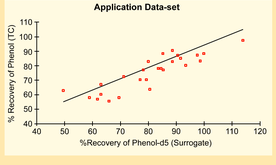
- Initially, focus on one target compound (phenol) and its deuterated surrogate analog (phenol-d5).
- Develop an estimator for a "training data-set" (single-blind Performance Evaluation (PE) material analyzed by about 40 laboratories).
- Assess the effectiveness of this estimator in an "application data-set" (single-blind PE material analyzed by 25 laboratories).
- Demonstrate the effectiveness of the bias estimator by "correcting" the bias in an application set.
- Investigate the applicability of this technique to additional target-surrogate compound combinations.

3 Results & Discussion

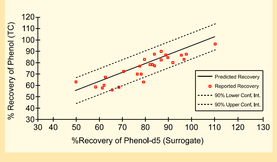
Phenol & Phenol-d5



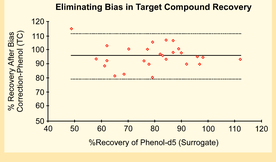
- Phenol and phenol-d5 recoveries are correlated in the training data-set (correlation coefficient 0.810).



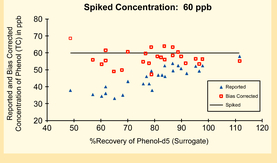
- Phenol and phenol-d5 recoveries are correlated in the application data-set (correlation coefficient 0.876).



- The regression line derived from the training data-set is clearly a good fit for the application data-set.



- Each data point in the application data-set is "corrected" for its bias (dividing by predicted recovery).

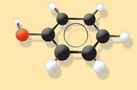


- The bias correction is applied to demonstrate the effectiveness of bias estimates (not recommended for routine application).

Mean Recovery Before & After Bias Correction

Before Correction	After Correction
75.2%	95.2%
16.0% RSD*	8.4% RSD*

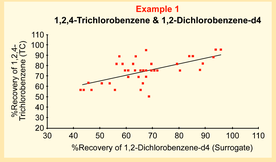
** Relative Standard Deviation*



- The bias is nearly eliminated and analytical imprecision is reduced by a factor of two (approximately).
- Further work using large data-sets is needed, therefore bias correction is not recommended at this time.

4 Other Target & Surrogate Compounds

- Is this concept applicable to other surrogate and target compounds?
- Examples are provided where surrogate compounds are not labeled analogs of target compounds.

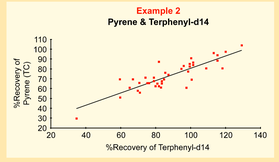


- The target and surrogate compound recoveries are fairly well correlated (correlation coefficient 0.644).
- For correlations of less than 0.500, this method may not be applicable.
- The bias corrected estimate of 1,2,4-trichlorobenzene recovery can be obtained from 1,2-dichlorobenzene-d4 recovery.

Example 1

Target Compound: *1,2,4-trichlorobenzene*

Surrogate Compound: *1,2-dichlorobenzene-d4*



- The target and surrogate compound recoveries are well correlated (correlation coefficient 0.863).
- The bias corrected estimate of pyrene recovery can be obtained from terphenyl-d14 recovery.

Example 2

Target Compound: *pyrene (fused-rings polyaromatic hydrocarbon)*

Surrogate Compound: *terphenyl-d14 (separated rings)*

5 Summary & Conclusions

- Useful estimates of target compound accuracy may be provided through proper interpretation of surrogate recoveries.
- It is possible to nearly eliminate analytical bias and to simultaneously reduce analytical imprecision by a factor of two (approximately).
- This approach may be used to replace other, more costly, QC procedures.
- This approach could be improved further by using additional surrogates selected for this specific purpose, and through the use of multiple surrogates.